Ethanol-selective catalytic reduction of NO by Ag/Al$_2$O$_3$ catalysts: Activity and deactivation by alkali salts

Leonhard Schill [a,b], Siva Sankar Reddy Putluru [a,b], Casper Funk Jacobsen [a,b], Christian Houmann Hansen [a,b], Rasmus Fehrmann [b], Anker Degn Jensen [a,*]

[a] Combustion and Harmful Emission Control Research Centre, Department of Chemical and Biochemical Engineering, Building 229, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark
[b] Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Building 207, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

ABSTRACT

Ag/Al$_2$O$_3$ catalysts with and without potassium doping were prepared by incipient wetness impregnation and characterized by N$_2$ physisorption, XRPD, NH$_3$-TPD and SEM. The influence of the Ag content from 1 to 5 wt.% was investigated for the selective catalytic reduction (SCR) of NO with ethanol. The 3 wt.% Ag/Al$_2$O$_3$ catalyst was found to be the most active and CO$_2$ selective over a wide temperature window (300–500 °C). Addition of 500 ppm of H$_2$ has a mild promotional effect on the activity while SO$_2$ has a strong negative influence on the SCR activity. Furthermore, the Ag/Al$_2$O$_3$ ethanol-SCR catalyst deactivated significantly by the addition of potassium although it was more resistant than the conventional V$_2$O$_5$ based NH$_3$-SCR catalyst, which deactivated more at lower potassium loading. The higher potassium resistivity of the Ag/Al$_2$O$_3$ catalysts seems to be due to differences in reaction mechanism of Ag/Al$_2$O$_3$ ethanol-SCR catalyst compared to the conventional NH$_3$-SCR catalyst. The still low potassium resistance, in combination with the high sensitivity to SO$_2$, seems not to make these catalysts a real option for biomass fired boilers.

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1. Introduction

The selective catalytic reduction (SCR) of nitrogen oxides is an important process in the avoidance of harmful emissions from stationary and mobile sources [1–6]. The process is currently being used extensively to reduce NO$_x$ from stationary sources with NH$_3$-SCR (especially power plants) with increasing attention for reduction of NO$_x$ from automotive vehicles by hydrocarbon based SCR (HC-SCR) and NH$_3$-SCR processes.

The selective catalytic reduction by ammonia is currently the most widespread method for the cleanup of NO$_x$ in flue gases from stationary sources by using V$_2$O$_5$–WO$_3$/TiO$_2$ catalysts. However, there are some drawbacks in terms of toxicity of vanadium, catalyst deterioration, NH$_3$-slip, ash odor and ammonia sulfate formation. There is therefore a desire to develop new catalysts operating in a wider temperature range and it is attractive to substitute ammonia by another reductant because of the dangers of storage, leakage, transport of liquid ammonia and ammonia sulfate formation on the catalyst which leads to poor performance [7–10]. These drawbacks can be overcome with hydrocarbon reductants using a suitable catalyst. The selective catalytic reduction of NO with hydrocarbons has been studied thoroughly in the last years as a possible competitor for the commercial NH$_3$-SCR process [5,11].

Since the discovery of the HC-SCR technology, various types of catalysts have been reported, such as ion-exchanged zeolites [5,7,11], supported precious metals [5,11], and metal oxide-based catalysts [12–15]. All the above mentioned catalysts have their advantages and disadvantages for practical use. Metal oxide-based catalysts show high stability and moderate tolerance to SO$_2$ and water vapor and in this context, Ag/γ-Al$_2$O$_3$ catalysts have been proposed. However, the development of an industrial HC-SCR technology has not yet been possible and the most significant reason is that no suitable catalytic system has been found exhibiting high selectivity to N$_2$ and CO$_2$, wide operational temperature performance, and high tolerance of SO$_2$ [5,7,11].

Several studies indicate that Ag/Al$_2$O$_3$ is a promising catalyst, showing a high efficiency in NO$_x$ reduction with hydrocarbons in excess oxygen [12–15]. Applied in stationary sources the cost and availability of the reductant is very important. Recently Lee et al. [13] investigated Ag/Al$_2$O$_3$ catalyst with a wide variety of hydrocarbon reductants ranging from C$_2$ to C$_{12}$ chain length. Among all the reductants ethanol showed the highest NO reduction activity in a wide temperature range. Shimizu et al. [14] found the following order for the NO$_x$ conversion by different hydrocarbons: ethers > alcohols > aldehydes > esters > ketones ≫ C$_3$H$_8$.

* Corresponding author. Tel.: +45 45252841; fax: +45 45882258.
E-mail address: aj@kt.dtu.dk (A.D. Jensen).

Biomass residues such as straw and wood are increasingly used as fuels and co-fuels at stationary sources such as power plants [16,17]. One of the major problems arising from the use of biomass is the deactivation of the V_2O_5–WO_3/TiO_2 based SCR catalyst by alkali metals, especially potassium, which the biomass contains in relatively large amounts [17]. Potassium deactivates the V_2O_5–WO_3/TiO_2 SCR catalyst by irreversibly binding to the V—OH Brønsted acidic sites, which are responsible for the ammonia adsorption, thus decreasing both their number and activity in NO reduction [18,19]. So far, the strategies to make the NH_3-SCR catalyst more alkali resistant have been: Adding sacrificial acidic sites (e.g. sulphated zirconia); increasing initial activity by using high loading of nano V_2O_5 on high surface TiO_2; using other active species (e.g. Cu/Zeolites) [20].

Another approach concerns development of deNO$_x$ catalysts functioning by a different mechanism that may be non- or less alkali sensitive. It is known from the literature that the HC-SCR mechanism involve activation of NO and the hydrocarbon by coordination to the Lewis acid sites of the active metal oxides distributed on the carrier surface, thus not involving the Brønsted sites mentioned above being active in the NH_3-SCR. Therefore, catalysts functioning with hydrocarbons as reductants in SCR of NO$_x$ may possibly be less sensitive to potassium salts in the flue gas, displaying a longer lifetime in biomass fired power plants. Typically, HC-SCR mechanisms are classified into two categories. One is the adsorption/dissociation mechanism (noble metal and Cu-zeolite catalysts) and the second one is the oxidation-reduction mechanism (metal oxide catalysts such as Ag/Al_2O_3, Sn/Al_2O_3 and In/Al_2O_3) [5]. This mechanistic advantage compared to NH_3-SCR would potentially increase the potassium resistance of the HC-SCR catalyst. The postulated reaction mechanism of ethanol-SCR using the Ag/Al_2O_3 catalyst apparently involves formation of both adsorbed nitrates (via NO oxidation by O_2) and enolic/acetate species (via the partial oxidation of ethanol). Further reaction between the nitrates and enolic/acetate species then leads to the formation of —NCO, which reacts with NO + O_2 and nitrates to yield N_2 [5,15]. Since ethanol-SCR is also comparatively active by HC-SCR standards, this combination of reductant and catalyst could be a potential substitute for NH_3-SCR using the V_2O_5–WO_3/TiO_2 catalyst at power stations firing biomass.

The catalysts used for the SCR process should be highly selective, particularly with respect to SO_2 oxidation. SO_2 levels can be decreased when firing with biomass since they contain relatively less sulphur compared to coal. The effect of SO_2 on various catalysts was examined by Okazaki et al. [21] concluding that the deactivation is a function of catalyst and reductant. Abe et al. [22] noted that silver sulfate decomposes at a lower temperature (427 °C) than aluminum sulfate (727 °C). Catalysts tested in their studies maintained their activity in the presence of SO_2 at higher temperatures (>427 °C) but tend to be inactive at temperatures lower than this.

In the present work, we report the influence of alkali and sulphur on the performance of Ag/Al_2O_3 SCR catalyst using ethanol as a reductant for biomass fired SCR application without compromising the activity, selectivity and also most importantly working within the desired SCR operating temperature region.

2. Experimental

2.1. Catalyst preparation and characterization

Ag/Al_2O_3 (Ag = 1–5 wt %) catalysts were prepared by incipient wetness impregnation of 180–300 μm γ-Al_2O_3 (Saint-Gobain, 256 m^2/g) particles with aqueous $AgNO_3$ (Sigma–Aldrich 99.0%) solutions. The catalysts were dried at 120 °C for 2 h and then calcined for 5 h at 550 °C. The 3 wt % Ag/Al_2O_3 catalyst was poisoned by

impregnating it with aqueous KNO_3 (Sigma–Aldrich, 99.99%) solutions to yield K concentrations of 139, 278, 417 and 556 μmol/g corresponding to K/Ag molar ratios of 0.5, 1.0, 1.5 and 2.0. The poisoned catalysts were also dried at 120 °C for 2 h and then calcined for 5 h at 550 °C.

X-ray powder diffraction (XRPD) measurements were performed on a Huber G670 powder diffractometer using CuK_α radiation within a 2θ range of 2–100° in steps of 0.02°. BET surface areas of the samples (100 mg of catalyst) were determined from nitrogen physisorption measurements at liquid nitrogen temperature with a Micromeritics ASAP 2010 instrument.

NH_3-TPD experiments were conducted on a Micromeritics Autochem-II instrument. In a typical TPD experiment, 100 mg of dried sample was placed in a quartz tube and pretreated in flowing He at 500 °C for 2 h. Then, the temperature was lowered to 100 °C and the sample was treated with anhydrous NH_3 gas (Air Liquide, 5% NH_3 in He). After NH_3 adsorption, the sample was flushed with He (50 ml/min) for 100 min at 100 °C. Finally, the TPD operation was carried out by heating the sample from 100 to 500 °C (10 °C/min) under a flow of He (50 ml/min).

The distribution of silver and potassium in the catalysts was investigated by using SEM-EDX on a LEO 440 microscope. The samples were prepared using an MT-990 rotary microtome. Before analysis, the samples were covered with a very thin carbon film to become conductive. To compare the different spectra and samples, both carbon and oxygen were excluded from the analysis and the amount of other elements was recalculated on a carbon and oxygen free basis.

2.2. Catalytic activity measurements

The SCR activity measurements were carried out at atmospheric pressure in a fixed-bed reactor loaded with 100–250 mg of fractionized (180–300 μm) catalyst at a flow rate of 3 NL/min (at room temperature). The inlet concentrations were: NO = 500 ppm, ethanol = 1000 ppm, H_2 = 0–500 ppm, SO_2 = 0–150 ppm, H_2O = 2% and O_2 = 5% with N_2 as balance gas. During the experiments the temperature was increased stepwise from 250 to 550 °C while the NO and NO_2 concentrations were continuously monitored by UV–vis (Eco Physics CLD 700 EL) analyzer. The CO and CO_2 concentrations were continuously monitored by a Rosemount NGA 2000 analyser and the N_2O with a Varian Micro GC CP-4900 using a PORAPLOT Q column. The activity was measured after attaining steady state (1 h) and care was taken not to reach 100% conversion to allow calculation of rate constants. Fresh and poisoned catalysts are compared by change in relative activity (%) of the corresponding catalysts. The ethanol concentration could not be measured directly, because ethanol was condensed out directly after the reactor, due to possible cross-sensitivity problems in the NO$_x$ analyzer. The ethanol conversion was estimated from the CO and CO_2 outlet concentrations. This may underestimate the true ethanol conversion due to the formation of intermediate oxidation products.

3. Results and discussion

The results of N_2-BET surface area and weight percentage of Ag are shown in Table 1. The bare support has higher surface area than the Ag/Al_2O_3 and potassium poisoned catalysts. With an increase in metal loading to Al_2O_3, a gradual decrease in surface area is noted. The X-ray powder diffraction (XRPD) patterns of Ag/Al_2O_3 catalysts are shown in Fig. 1. The presence of a dominating γ-Al_2O_3 phase was observed in all catalysts. No peaks attributable to Ag^0, Ag_2O, or $AlAgO_2$ phases were observed. This shows a good dispersion of the silver on the support. The detection limit of the XRPD apparatus is around 5 nm, and so any silver particles would be below this size.

Table 1
Physico-chemical properties of Ag/Al$_2$O$_3$ catalysts.

Catalyst	Ag (wt.%)	K/Ag (mol/mol)	Surface area (m^2/g)	Acidity (μmol/g)
γ-Al$_2$O$_3$	–	–	256	484
1 wt.% Ag/Al$_2$O$_3$	1.0	–	255	547
2 wt.% Ag/Al$_2$O$_3$	2.0	–	254	570
3 wt.% Ag/Al$_2$O$_3$	3.0	–	252	607
4 wt.% Ag/Al$_2$O$_3$	4.0	–	248	549
5 wt.% Ag/Al$_2$O$_3$	5.0	–	243	517
K/Ag – 0.5	3.0	0.5	250	478
K/Ag – 1.0	3.0	1.0	235	436
K/Ag – 1.5	3.0	1.5	231	365
K/Ag – 2.0	3.0	2.0	229	269

Fig. 2 shows the catalytic activity profiles of 1–5 wt.% Ag/Al$_2$O$_3$ catalysts as a function of reaction temperature. Fig. 2a shows that a gradual increase in Ag loading enhanced the NO conversion which reaches a maximum at 3 wt.% Ag while further increase of Ag loading leads to a gradual decrease of NO conversion. At the low temperature range below 300 °C, the catalysts exhibited low activity and appreciable activity was only observed between 350 and 500 °C. These results are similar to those reported in the literature with temperature window ranging from 300 to 500 °C for 2–3 wt.% Ag/Al$_2$O$_3$ catalysts [12,13,23]. The highest NO conversions were observed at silver loadings of 2 and 3 wt.% Ag/Al$_2$O$_3$, both at 400 °C. An optimum content at 3 wt.% Ag in the catalyst was observed with a maximum NO conversion of 96% at 400 °C. Note that there is no formation of N$_2$O for all the catalysts in the given temperature range. The Ag loading of 2 wt.% has been widely accepted as the optimal Ag content for the HC-SCR technology [5]. However, the optimum Ag content of the Ag/Al$_2$O$_3$ catalyst seems to vary depending on the catalyst preparation method (affect the Ag oxidation state and particle size), support surface area and type of reductant employed [5,7,23]. Fig. 2b and c shows the ethanol conversion and CO$_2$ selectivity profiles of 1–5 wt.% Ag/Al$_2$O$_3$ catalysts as a function of reaction temperature. With increasing Ag content from 1 to 5 wt.% the ethanol conversion and CO$_2$ selectivity increases steadily. 3 wt.% Ag is mild in ethanol conversion and maintained above 80% CO$_2$ selectivity. The 3 wt.% Ag/Al$_2$O$_3$ catalyst was chosen for further experiments, because of higher NO conversions at lower temperatures (300–350 °C), mild ethanol conversion and slightly lower CO emissions. Generally, higher silver loading leads to high hydrocarbon conversion [5,24]. The optimum ethanol-SCR activity of the 3 wt.% Ag/Al$_2$O$_3$ catalyst can be partly explained
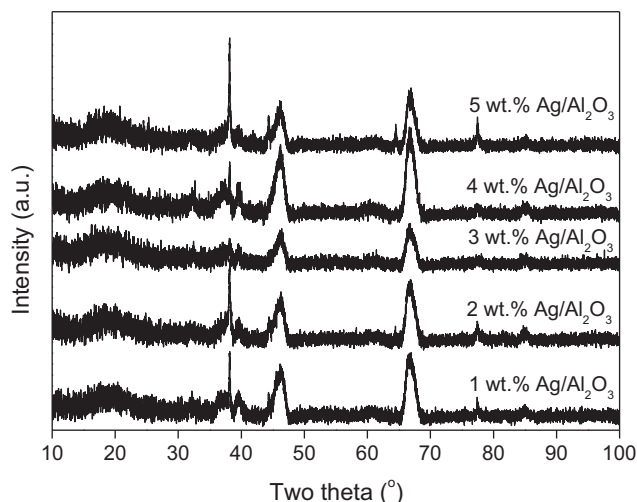

Fig. 1. XRPD patterns of 1–5 wt.% Ag/Al$_2$O$_3$ catalysts.
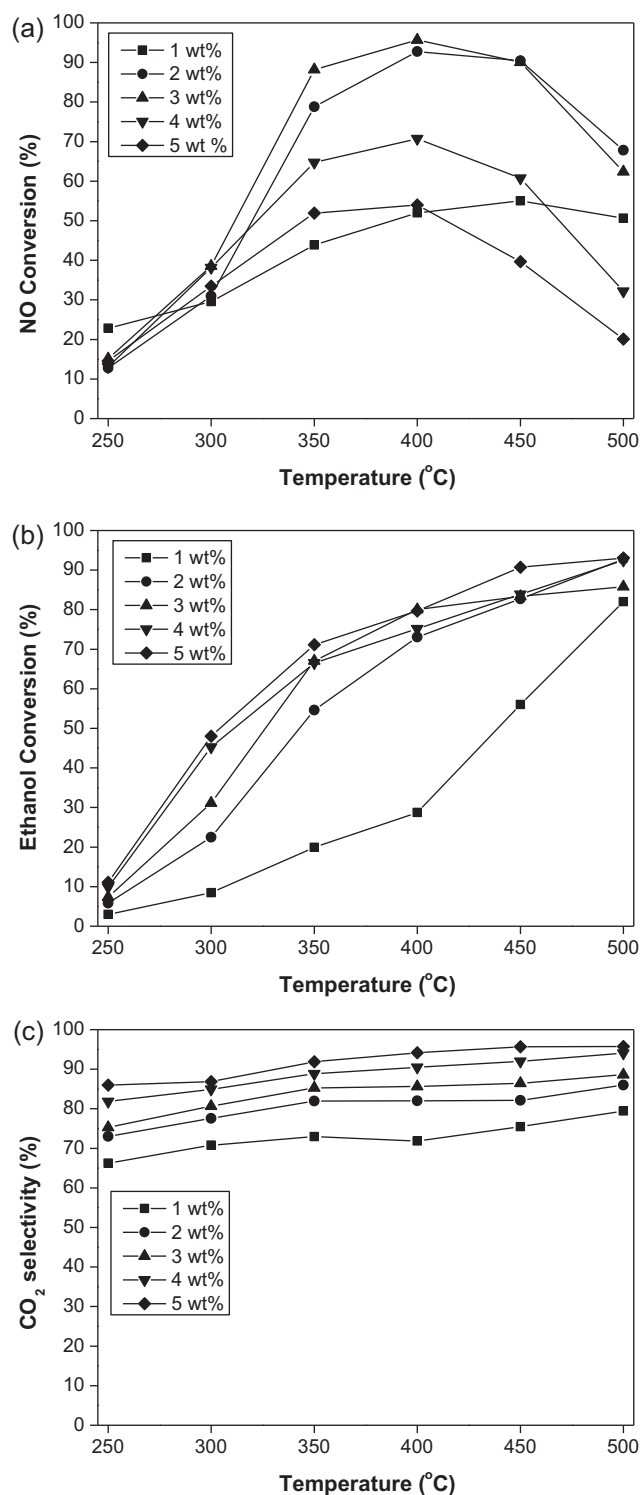

Fig. 2. NO conversion (a), ethanol conversion (b) and CO$_2$ selectivity (c) for 1–5 wt.% Ag/Al$_2$O$_3$ catalysts. Reaction conditions: SV = 720,000 N ml/(g h); 500 ppm NO, 1000 ppm ethanol, 5% O$_2$, 2% H$_2$O, balance N$_2$.

by the physico-chemical properties of the catalysts displayed in Table 1. The 3 wt.% Ag/Al$_2$O$_3$ catalyst was found to be the most acidic among all catalysts and the attained surface area close to the Al$_2$O$_3$ support.

Fig. 3 shows the influence of H$_2$ on ethanol-SCR activity of the 3 wt.% Ag/Al$_2$O$_3$ catalyst at 400 °C. H$_2$ has proven to enhance the conversion of NO and reductants [7,14,25,26]. One of the reasons for the enhanced activity of H$_2$ is attributed to the favored
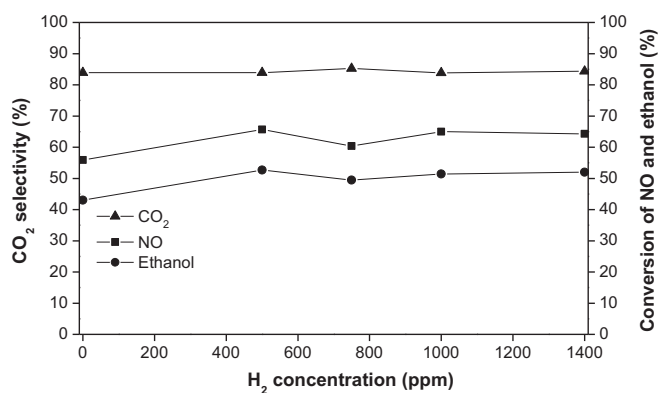
Fig. 3. NO conversion, ethanol conversion and CO_2 selectivity as a function of H_2 concentration at 400 °C on 3 wt.% Ag/Al_2O_3 catalyst. Reaction conditions: SV = 1,800,000 N ml/(g h); 500 ppm NO, 1000 ppm ethanol, 0–1400 ppm H_2, 5% O_2, 2% H_2O, balance N_2.

Fig. 4. NO conversion, ethanol conversion and CO_2 selectivity as a function of SO_2 concentration at 400 °C on 3 wt.% Ag/Al_2O_3 catalyst. Reaction conditions: SV = 1,800,000 N ml/(g h); 500 ppm NO, 1000 ppm ethanol, 0–150 ppm SO_2, 5% O_2, 2% H_2O, balance N_2.

formation of important species such as acetate and NCO species, whose formation is viewed as the rate-determining step in the absence of H_2 [25–27]. Shimizu et al. [14] have tested the effect of 0.5 vol.% H_2 on various hydrocarbon reductants over wide ranges of temperatures and found that the NO conversion is enhanced at lower temperatures. To monitor the changes in conversion levels the conversion was decreased by increasing the space velocity from 720,000 to 1,800,000 N ml/(g h). The addition of 500 ppm of H_2 to the ethanol leads to an increase in NO conversion from 56% to 66% and the ethanol conversion is also increased from 43% to 51%. Further increase in H_2 does not have a significant impact on the conversion levels. The ethanol conversion values (calculated from the CO and CO_2 concentrations) are relatively lower than the NO conversion at low reaction temperatures (Fig. 2). It indicates that NO is reduced while the ethanol is oxidized to intermediate products [27], as reported in the literature where acetaldehyde formation is observed between 100 and 300 °C on a 3 wt.% Ag/Al_2O_3 catalyst [28]. Further, an increase in acetaldehyde formation was also observed in the presence of H_2. The CO_2 selectivity is not much affected by the presence of H_2. Most of the previous investigations were done at comparatively high H_2 concentrations (0.2–1 vol.%) [7,14,25]. However, high H_2 concentrations may have less practical applications in industrial power plants due to cost and safety issues. The present results show that 500 ppm of H_2 is sufficient to promote the ethanol-SCR activity and more attractive for industrial purpose.

The influence of SO_2 in concentrations of 25, 50, 100 and 150 ppm, at 400 °C is shown in Fig. 4. The catalytic performance of the 3 wt.% Ag/Al_2O_3 catalyst is very strongly affected by the presence of SO_2 in the flue gas. The results show that a large drop in conversion, from 56% to 26%, happened from 0 to 25 ppm of SO_2. A further increase to 50 ppm of SO_2 still reduced the conversion, down to 21% but as the concentration was further increased to 100 and 150 ppm the slope flattens out to 17% and 16%, respectively. It should be noted that the ethanol conversion decreases by about the same factor as the NO conversion. This indicates that SO_2 merely decreases the number of active sites but does not alter the reaction mechanism. The CO_2 selectivity, however, decreases drastically with increasing SO_2 concentration up to 150 ppm indicating a change in a part of the mechanism. He et al. [15] have studied the influence of 80 ppm of SO_2 on the NO_x conversion for various hydrocarbon reductants using a 4 wt.% Ag/Al_2O_3 catalyst. Ethanol showed a much higher resistance towards SO_2 (NO conversion changed from 98% to 93% only) than other reductants at 50,000 h^{-1} GHSV. In the present investigation the severe deactivation of 25 ppm SO_2 (NO conversion changed from 56% to 26%) is
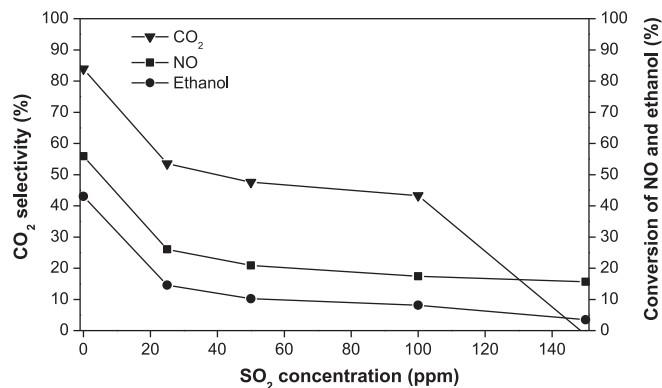
observed at a high space velocity of 1,800,000 N ml/(g h). The poisoning mechanism by SO_2 could be that SO_2 reacts with oxides on the catalyst surface to form stable sulfates (silver sulfate and aluminum sulfate) under reaction conditions. The formation of stable sulfate species results in a reduced number of sites for chemisorption of NO [5,22]. Since flue gases from purely biomass-fired boilers may contain up to 100 ppm of SO_2, increasing the SO_2 tolerance of alumina based catalysts will be of utmost importance.

3 wt.% Ag/Al_2O_3 catalyst was investigated under the influence of 500 ppm of H_2 and 60 ppm SO_2 gases (Fig. 5). It was observed that the addition of 500 ppm of H_2 enhanced the overall conversion of NO and the conversion pattern was similar to that of the pure ethanol-SCR. At low temperatures the NO conversions of the pure catalyst were low and the addition of hydrogen showed positive effect, though still at a low degrees of conversion. At the optimum temperature of 400 °C, the degree of conversion was shifted from 56% to 66% under the influence of 500 ppm of H_2. When introducing SO_2 into the H_2–ethanol–SCR system, a dramatic loss of activity was observed. The maximum conversion was reached at a relatively high reaction temperature (500 °C) and maximum conversion of NO dropped from 66 to 25%. Overall, presence of 500 ppm of H_2 gas slightly promotes the ethanol-SCR and 60 ppm of SO_2 gas deactivates the catalyst even in the presence of H_2.
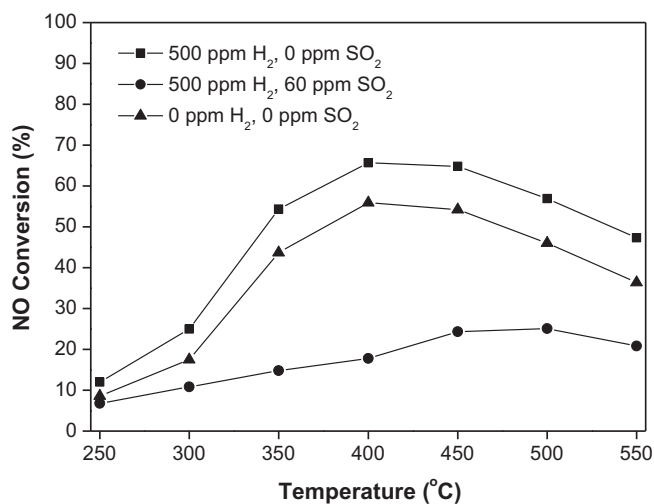

Fig. 5. Effect of H_2 and SO_2 on 3 wt.% Ag/Al_2O_3. Reaction conditions: SV = 1,800,000 N ml/(g h); 500 ppm NO, 1000 ppm ethanol, 0–500 ppm H_2, 0–60 ppm SO_2, 5% O_2, 2% H_2O, balance N_2.

(a)

Fig. 7. Effect of H_2 and SO_2 on potassium poisoned 3 wt.% Ag/Al_2O_3 catalyst (K/Ag – 0.5). Reaction conditions: SV = 720,000 N ml/(g h); 500 ppm NO, 1000 ppm ethanol, 0–500 ppm H_2, 0–60 ppm SO_2, 5% O_2, 2% H_2O, balance N_2.
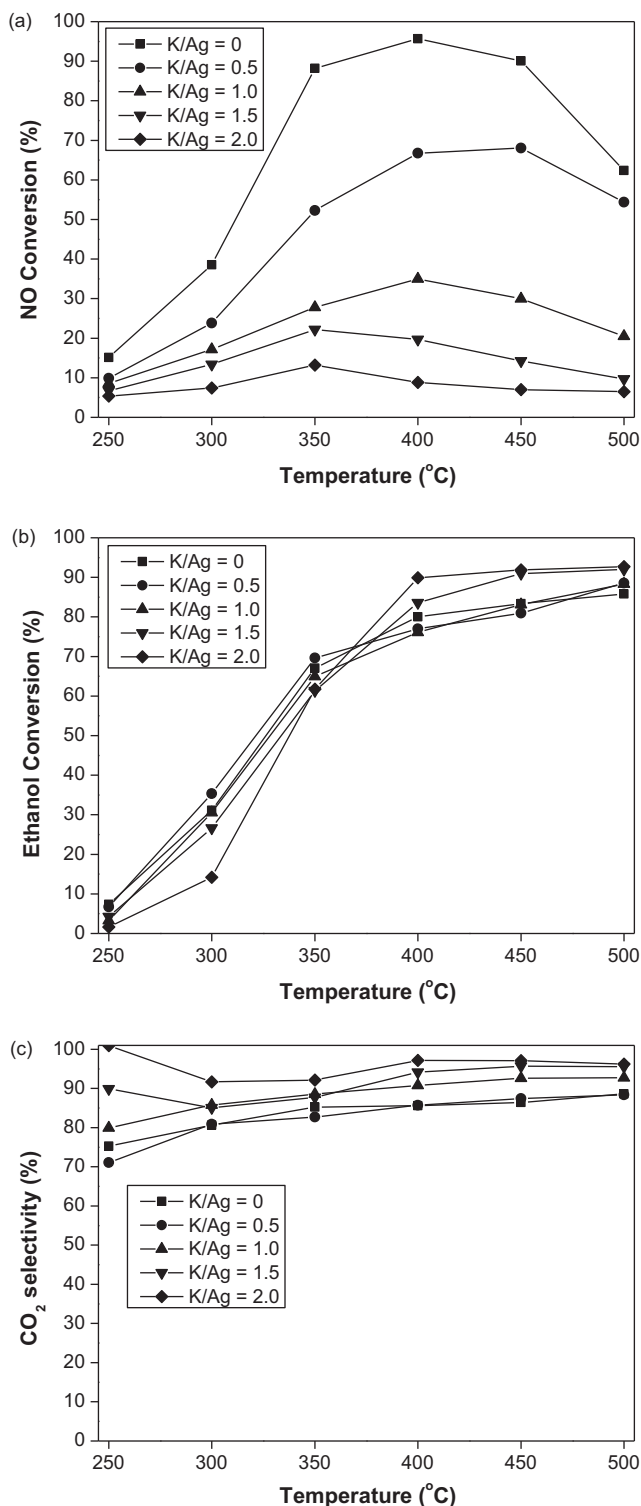
(b)

(c)

Fig. 6. NO conversion (a), ethanol conversion (b) and CO_2 selectivity (c) for potassium poisoned 3 wt.% Ag/Al_2O_3 catalysts. Reaction conditions: SV = 720,000 N ml/(g h); 500 ppm NO, 1000 ppm ethanol, 5% O_2, 2% H_2O, balance N_2.

Deactivation of 1 wt.% V_2O_5–7 wt.% WO_3/TiO_2 catalyst at a biomass fired power plant showed an average concentration of K/V (mol/mol) up to 2 [18]. In the present investigation the potassium concentration was also studied up to K/Ag (mol/mol) concentration of 2. Doping the optimum 3 wt.% Ag/Al_2O_3 catalyst with potassium (K/Ag = 0.5–2.0) resulted in a gradual decrease in NO conversion (Fig. 6). The results show that a molar ratio of K/Ag = 0.5, decreased
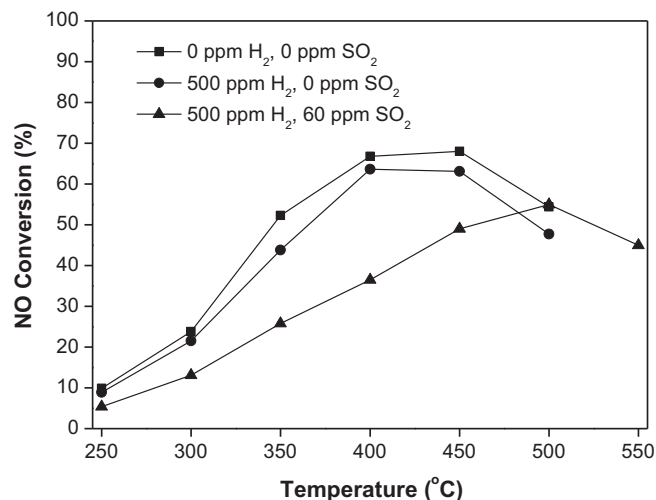
the maximum NO conversion from 96% to 67%. Further addition of potassium to a molar ratio of K/Ag = 1.0 decreased the maximum NO conversion to 35%. At the molar ratios of K/Ag = 1.5 and 2.0 the catalysts were almost completely deactivated, exhibiting maximum NO conversions of 22 and 13%, respectively. Fig. 6 also shows the ethanol conversion and CO_2 selectivity profiles of potassium poisoned Ag/Al_2O_3 catalysts as a function of reaction temperature. Compared to the potassium free 3 wt.% Ag/Al_2O_3 catalyst, K/Ag = 0.5 and 1.0 catalysts showed slightly increased or almost similar ethanol conversions below 350 °C and lower conversions above 350 °C while the conversion for the K/Ag = 1.5 and 2.0 catalysts showed the opposite trend. Regarding CO_2 selectivity, the catalysts showed higher CO_2 selectivity compared to 3 wt.% Ag/Al_2O_3 except for the K/Ag = 0.5 catalyst throughout the temperature window. 1 wt.% potassium on 2 wt.% Ag/Al_2O_3 catalyst also showed deactivation effect for SCR of NO with C_3H_6 [29].

The potassium doped 3 wt.% Ag/Al_2O_3 catalyst (K/Ag = 0.5) was further investigated under the influence of 500 ppm of H_2 and 60 ppm SO_2 gases (Fig. 7). The maximum conversion of K/Ag = 0.5 catalyst was determined to 68% at 450 °C, under normal ethanol-SCR conditions. Upon addition of 500 ppm hydrogen, the conversion profile followed the same pattern, however the conversion was slightly lower, i.e. 63% at 450 °C. Thus hydrogen addition seems to have no positive influence on the conversion of for the poisoned catalyst. When introducing SO_2 to the H_2-ethanol-SCR system, the conversion profile of the catalyst switched to higher temperatures reaching maximum NO conversion of 55% at 500 °C. Overall, there is no promotional effect of H_2 on poisoned K/Ag catalyst and SO_2 further decreases the NO conversion, probably by conversion of the Al_2O_3 carrier to $Al_2(SO_4)_3$.

The surface of the catalysts was investigated on a scale of 1 μm through scanning electron microscopy (SEM). Fresh and potassium poisoned Ag/Al_2O_3 catalysts were analyzed using SEM and the images are shown in Fig. 8. It was observed that the surface particles vary in shape and size depending on the Ag content. The 1 wt.% Ag/Al_2O_3 catalyst image is assumed to resemble the pure alumina surface, due to the low silver concentration on the surface. When increasing the silver content to 3 wt.%, the particles are found to be smaller and evenly distributed on the surface. By further increase of the silver content to 5 wt.% uneven particle sizes are observed with a rough surface. Furthermore, agglomeration of silver oxide is more common at the highest weight percentage resulting in larger particles. Potassium poisoned 3 wt.% Ag/Al_2O_3 catalyst (K/Ag = 1)
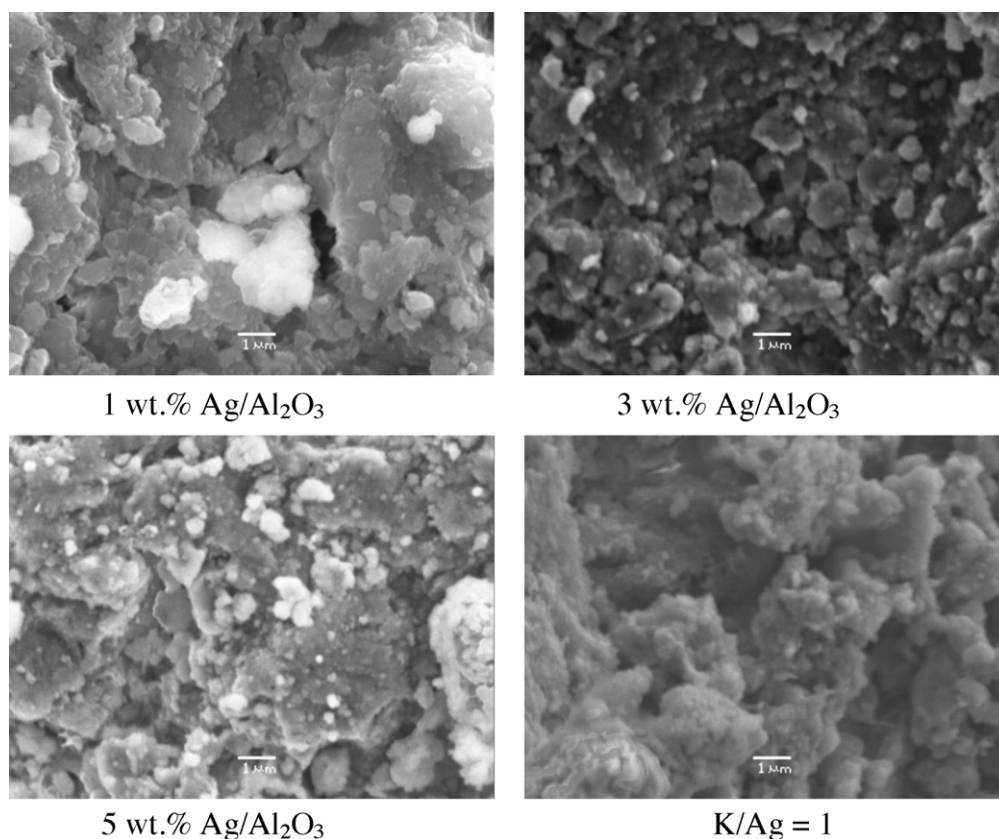
Fig. 8. SEM images of fresh and potassium poisoned Ag/Al_2O_3 catalysts.

showed rough surface with uneven particles, possibly caused by masking by the potassium on the catalyst surface.

The activity of a vanadia based NH_3-SCR catalyst ($3\,wt.\%\,V_2O_5$–$7\,wt.\%\,WO_3/TiO_2$) and ethanol-SCR catalysts was calculated in terms of a first order (in NO) rate constant at $400\,°C$ for different potassium loadings and the results are shown in Fig. 9 as the relative activity (k/k_0). The ethanol-SCR catalyst showed higher relative activity compared to the NH_3-SCR catalyst even at elevated potassium loadings. Table 1 shows the acidity of the potassium poisoned $3\,wt.\%\,Ag/Al_2O_3$ catalysts. The K/Ag – 0.5

catalyst showed almost stoichiometric acidity loss after doping with $139\,\mu mol/g$ of potassium. However, the NH_3-SCR catalyst showed above stoichiometric (≈ 5 times) acidity loss after doping with $100\,\mu mol/g$ of potassium [30]. Such a change in relative activity and acidity between the both processes reveal that potassium deactivation is milder on ethanol-SCR catalyst compared to NH_3-SCR catalyst, possibly due to the difference in reaction mechanism as discussed above.

4. Conclusions

In summary, Ag/Al_2O_3 catalysts are highly active and CO_2 selective in the ethanol-SCR of NO. Ag/Al_2O_3 catalysts exhibited higher resistance to alkali poisoning compared to the NH_3-SCR catalyst. $500\,ppm$ of H_2 has a mild promotional effect while SO_2 is severely deactivating the Ag/Al_2O_3 catalyst. The potassium doped catalysts did not exhibit any promotional effect by H_2 which instead slightly decreased the NO conversion. Overall, the presently investigated Ag/Al_2O_3 catalysts do not seem robust enough to be a real option for SCR on biomass fired boilers.

Acknowledgments

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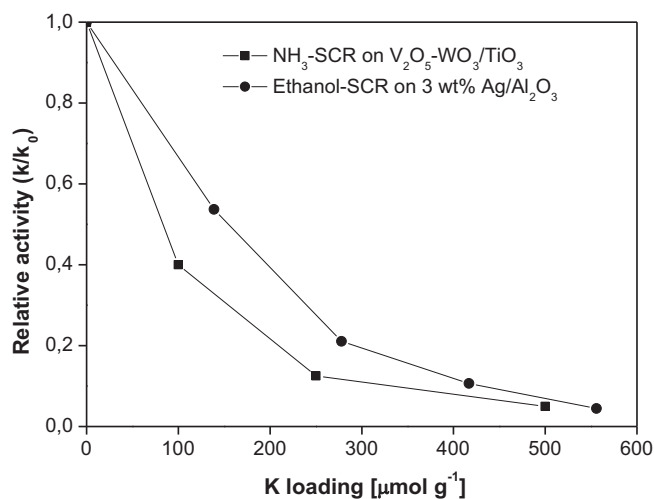[5] Z. Liu, S.I. Woo, Catal. Rev. 48 (2006) 43.

Fig. 9. Relative activity of $3\,wt.\%\,V_2O_5$–WO_3/TiO_2 catalyst and $3\,wt.\%\,Ag/Al_2O_3$ catalyst at various potassium concentrations at $400\,°C$. k, k_0 represent first order rate constants ($cm^3/g\,s$) of potassium poisoned and fresh catalysts, respectively.

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